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The kinetics of reactions in Ag/Al thin film couples

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Abstract : Differential scanning calorimetry has been used to follow the kinetics of reactions in thin bilayer films of Ag and Al producing a single phase product of Ag_2Al. From the analysis of the shifts of two minima appearing in the calorimetry curves with films having different heating rates, the activation energies of the formation of the phase along and perpendicular to the interface have been found to be 0.98 and 0.93 eV respectively.

Keywords : Differential scanning calorimetry, bilayer films, phase transformations, activation energy.

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Interdiffusion in thin films occurs much faster than in bulk materials because of high densities of defects such as dislocations, grain boundaries and vacancies. With the formation of intermetallic compound at the interface the diffusion process is further modified. Differential scanning calorimetry (DSC) is widely used to study thin film reaction kinetics. Kinetic data on the phase transformations can be obtained from the shape of transformation peaks as well as from the shift in the transformation temperatures with the scanning rate (Kissinger 1957 and Henderson 1979). We have chosen Ag/Al as a suitable system to be studied with DSC, because X-ray diffraction data shows that Ag/Al bilayered films when annealed at 373 K, only the peaks of elements appear but on annealing at 423 K the reaction proceeds to produce a single phase product of Ag_2Al (Roy and Sen 1991).

Films of Ag and Al (65 nm and 55 nm in thickness respectively) were deposited in-situ sequentially on freshly cleaned glass substrates under a high-vacuum of the order of 70 μ Pa in-situ. Films thus prepared were next removed from the substrate and thermal analysis were preformed in constant heating rate mode using Perkin-Elmer DSC 7 power compensated differential scanning calorimetry in nitrogen atmosphere to prevent oxidation. About 2 mg of sample was used for each DSC run and in all cases the samples were first allowed to stabilize at 322 K and then the heating was initiated. The experiment performed on two sets of films having different thicknesses (65 nm Ag/55 nm Al and 95 nm Ag/100 nm Al) at the constant heating rate i.e., 20 K/min have been shown in Figure 1. Two

minima corresponding to the negative heat of reaction are found to appear in each case. Position of peak (1) does not appreciably change but that of peak (2) shifts to higher temperature as the film thickness increases. Peak heights are also seen to decrease with the increase of film thickness.

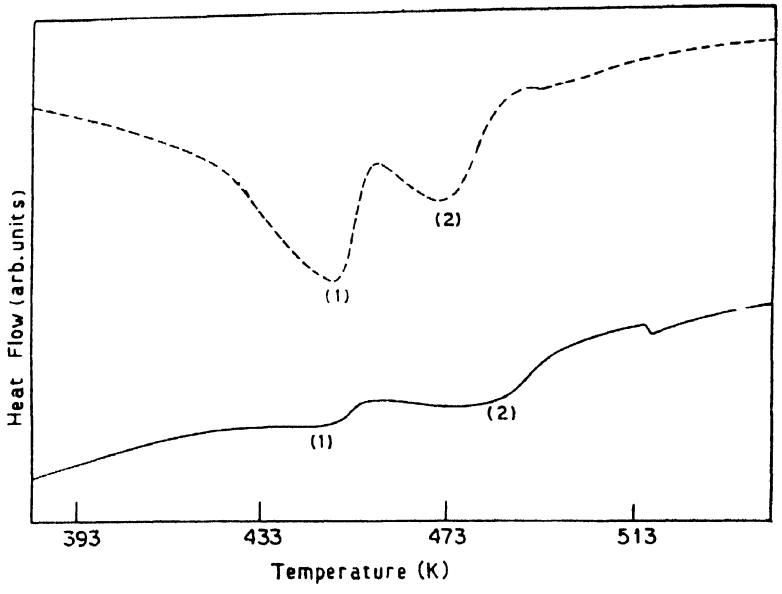

Figure 1. Differential scanning calorimetry curves of Ag/Al films for heating rate of 20 K/min (The dotted curve is for 65 nm Ag/55 nm Al films and the solid curve for 95 nm Ag/100 nm Al films, (1) and (2) correspond to two peak minima as explained in the text

The calorimetric curves with the first film for five different heating rates of 2 to 40 K/min have also been shown in Figure 2. Upon increasing the heating rate in the DSC scans both the peaks are observed to occur at progressively higher temperature indicating that the reaction process is thermally activated. This shift with increasing scanning rate can be related to the activation energy by the following expression (Kissinger 1957)

$$\ln [H / T_p^2] = C_2 - Q / kT_p \quad (1)$$

where H is the heating rate, T_p, the peak temperature, C_2 is a constant, K, the Boltzmann constant and Q, the activation energy of reaction.

$\ln [H / T_p^2]$ has been plotted against $1/T_p$ in Figure 3 and from the root mean square fitting of the above plot, Q has been found to be 0.98 and 0.93 eV for peak (1) and peak (2) respectively. As the position of peak (2) for the scanning rate of 2 K/min is uncertain, this has been omitted for the corresponding Q calculation.

In order to understand the DSC traces of the films the model proposed by Coffey *et al* (1989) can be applied. There are two extrema in the reaction rate during the formation of

single product phase of Ag_2Al. The first extremum can be interpreted as being due to the inhomogenous formation of the product phase at the initial reactant layer interface by nucleations at many locations. Here the interfacial area rather than the layer thickness is being consumed. But with time the interfacial area is reduced and a continuous product layer is formed. The second extremum corresponds to the completion of the reaction due to the

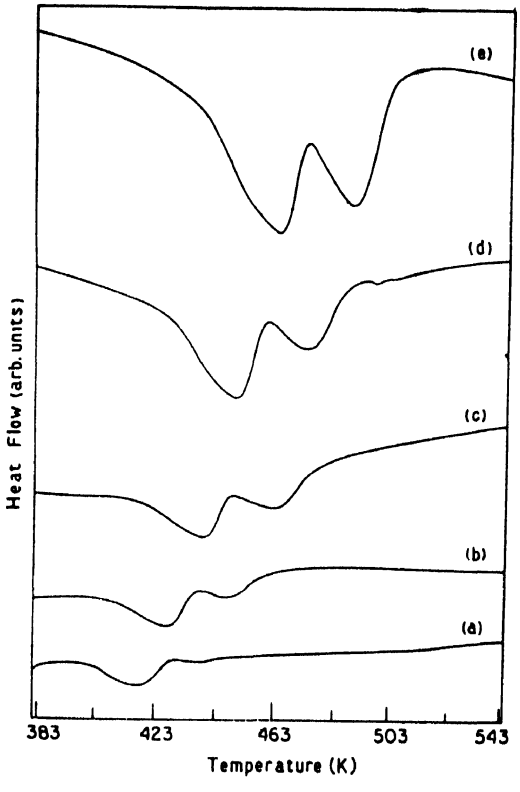

Figure 2. DSC traces of 65 nm Ag/55 nm Al films for heating rates (a) 2 K/min, (b) 5 K/min, (c) 10 K/min, (d) 20 K/min and (e) 40 K/min.

consumption of one or both reactant layers. Thus the two activation energies (Q) measured above correspond to the formation of Ag_2Al phase along and perpendicular to the interface. An average "Q" value of 0.95 eV as measured from the peak shifts of the two peaks described above can only be compared with an independent experiment performed by Baglin *et al* (1978) using Rutherford back scattering (RBS) technique. The latter value which is 0.86 ± 0.05 eV seems to be slightly lower than our estimated value.

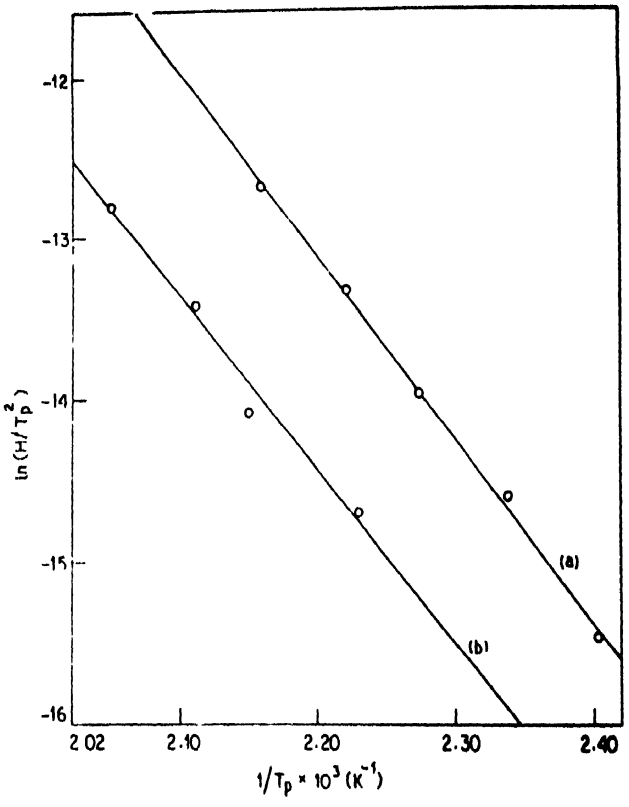

Figure 3. Kissinger plot for 65 nm Ag/55 nm Al bilayer films : (a) and (b) correspond to peak (1) and peak (2) respectively.

Acknowledgment

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